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## **Ionic liquid control crystal growth to enhance planar perovskite solar cells efficiency**

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Perovskite solar cells (PSCs) have had a lasting impression on the scientific community because of their fast progress as high efficient and low cost technology. Starting from the seminal work of Kojima and co-workers in 2009, in only 7 years power conversion efficiencies above 22% have already been reported and certified.<sup>[1-4]</sup> In aspect of economic and technological analysis, one promising route to industrialization of PSCs is to take advantage of the complementary band gaps of perovskite and silicon solar cells, *i.e.* to create a perovskite-silicon tandem. In a tandem architecture the perovskite can be deposited on the top of bottom cell to potentially overtake the Shockley Queisser limitation for a single junction device.<sup>[5]</sup> This strategy is promising, but it requires low-temperature processing (100°C) to avoid damaging of the bottom silicon cell. Currently, the highest efficient PSCs employ a mesoscopic TiO<sub>2</sub> electron contact, which is processed at temperature above 400°C

and thus not compatible with the preparation of tandem devices. Although there are strategies to prepare mesoscopic  $\text{TiO}_2$  at low temperature, the easiest approach would be to use a planar perovskite device without mesoporous layer.<sup>[6]</sup> We recently demonstrated low temperature processed  $\text{SnO}_2$  as electron contact in planar PSCs for tandem silicon-perovskite solar cell.<sup>[7]</sup> Although the efficiency of our tandem device was one of the highest reported, the top planar PSC was poorly performing compared to a mesoscopic  $\text{TiO}_2$  based device. Therefore, to profit from using perovskite in tandem with other photovoltaic materials, planar devices need to be improved.

In planar PSCs, the crystallinity, morphology, thickness, and surface coverage of perovskite film are critical for the device performance.<sup>[8]</sup> Several methods have been proposed to prepare high-quality perovskite layer, such as spin-coating, two-step sequential deposition, and vacuum vapor deposition.<sup>[3, 9-12]</sup> Even though the one-step spin-coating method enabled among the highest efficiencies, the perovskite films frequently showed poor surface coverage, which result in a reduced cell performance.<sup>[13]</sup> To overcome these issues, control of perovskite crystal growth and morphology has been widely investigated using several additives in the perovskite precursor solution.<sup>[14-16]</sup> Shahiduzzaman *et al.* made use of the low vapor pressure ionic liquid (IL) 1-hexyl-3-methylimidazolium chloride to control the film morphology by forming a uniform distribution of perovskite nanoparticles.<sup>[16]</sup> Moore *et al.* demonstrated that methylammonium formate can be used as an additive to produce higher quality, crystalline perovskite films.<sup>[15]</sup> Although these studies suggested that adding ILs in the perovskite precursor solution may help to prepare better solar cells, there are currently no reports that implemented this strategy to improve state-of-the-art planar PSCs.

In this work, we demonstrate that ionic liquids enable the highest ever reported stabilized power conversion efficiency for a planar perovskite solar cell. We show that compact perovskite films with larger crystalline domain can be prepared from solution by adding particular ionic liquids, such as methylammonium formate, to the precursors. We

demonstrate that larger crystalline domains result in a more effective charge collection and thus better photovoltaic performances. We propose an IL driven mechanism of crystallization as a new strategy to prepare highly efficiency planar perovskite solar cell.

Ionic liquids (ILs) are well known for their extremely low vapor pressure, which makes them non-volatile liquids. If added in small amount (few mol%) in the precursor solution, they remain in the perovskite film after all the solvent has evaporated during the annealing.<sup>[15,16]</sup> For this study we focused on the IL methylammonium formate (MAF), owing to its affinity with the perovskite precursor methylammonium iodide (MAI).<sup>[17]</sup> The chemical structures of MAF and MAI are shown in Figure 1a. They have the same cation (methylammonium) and a different counter anion, formate ( $\text{HCOO}^-$ ) or iodide ( $\text{I}^-$ ). Since  $\text{HCOO}^-$  is known to form metal-organic complex with  $\text{Pb}^{2+}$ , our working hypothesis was that the  $\text{HCOO}^-$  influences the crystal growth of the perovskite interacting with  $\text{Pb}^{2+}$ .<sup>[18]</sup> In Figure 1b, we depict a schematic view of the proposed mechanism: STEP 1)  $\text{HCOO}^-$  coordinates with  $\text{Pb}^{2+}$  in solution and during the early stage of the crystal growth; STEP 2) the complex  $\text{HCOO}^- \cdot \text{Pb}^+$  is gradually displaced by  $\text{Pb}^+ \cdot \text{I}^-$  when films are heated to 100 °C; STEP 3)  $\text{HCOO}^- \cdot \text{Pb}^+$  coordination is completely replaced by  $\text{Pb}^+ \cdot \text{I}^-$  enabling the crystal growth. Once the crystallization is completed MAF sits at the surface of the perovskite crystals as schematically presented in the left hand side of Figure 1b.

To investigate the impact of the MAF on the crystal growth, we prepared perovskite precursor solutions with and without 5mol% of MAF. Perovskite films were prepared on  $\text{SnO}_2$  deposited FTO substrates by spin coating the precursor solution in a nitrogen filled glovebox using the one-step anti-solvent method.<sup>[19]</sup> In Figure 2a we report the pictures of the perovskite films collected every 5s after posing the substrates on an hotplate at 100°C. It is evident that the film without MAF turns black earlier than the film with MAF. This simple experiment suggested that the crystal growth is slowed down by the presence of MAF. To look at the impact of the slower crystal growth on the film morphology, we collected scanning

electron microscopy (SEM) images of the film surface after the annealing was completed (1 hour at 100°C). SEM images of perovskite films show that the average grain sizes are 170 nm and 325 nm without and with MAF, respectively. Therefore, a slower crystal growth induced larger average grain size. More interesting, we notice that the MAF inhibits the formation of grains smaller than 150 nm, which represent a great portion of the size distribution in the film without the MAF (see statistical distribution in Figure 2b).

In order to investigate the impact of the MAF on the crystal structure of the perovskite, X-ray diffraction (XRD) patterns were collected from perovskite films with and without MAF on SnO<sub>2</sub> substrates. The XRD spectra in Figure 3a show that the MAF mediated perovskite is rather similar to the non-MAF film. This indicates that the HCOO<sup>-</sup> does not induce polymorphism or variation of the crystal lattice, even if it has a large influence on the perovskite film morphology, as shown in Figure 2. Furthermore, the fact that the diffraction pattern is the same, despite the size of HCOO<sup>-</sup> being larger than I<sup>-</sup> (HCOO<sup>-</sup> 249 Å > I<sup>-</sup> 220 Å), suggests that HCOO<sup>-</sup> is not incorporated in the perovskite crystal lattice.<sup>[17,20]</sup> It is interesting to note that the intensity of the peaks (112), (211), (202) and (224) relative to the intensity of the (110) peak (inset Figure 3a) is significantly higher in the film without MAF. This indicates a preferential crystal growth of (110) crystallite in presence of MAF. This result supports the change in morphology we observed with the SEM imaging, which showed that MAF induces larger grain size along the plane of the substrate (see Figure 2b and SI).

Planar perovskite solar cells (PSCs) with and without MAF in perovskite precursor solution were prepared on compact SnO<sub>2</sub>, following the procedures previously reported by Baena *et al.*<sup>[21]</sup> Figure 4a displays the current density-voltage (*J-V*) curves of the best PSCs with the corresponding metrics reported in Table 1. The data show that MAF improves the short circuit current density (*J<sub>sc</sub>*) by 1 mA cm<sup>-2</sup>. This is confirmed by the incident photon-to-current efficiency (IPCE) in Figure 4b. We notice that with and without MAF the integrated current density is lower than what is measured from the *J-V* curves. This trend has been

systematically observed also from other groups, and it can in part be attributed to a small spectral mismatch between the solar simulator and the standard AM 1.5 G emission.<sup>[19, 22]</sup> In Figure 4c we reported the statistical analyses (box plot) of the maximum PCE collected from 7 independent devices, which confirmed the improvement with MAF. To rule out the impact of the hysteresis on the estimated PCE, we tracked the device maximum power output for 5 minutes in order to extract the stabilized maximum PCE. Figure 4d displays that the PCE stabilizes after about 50s to 18.9% for the control and 19.5% for MAF device (see Table 1), confirming the values extracted from the J-V curves in Figure 4a. We want to highlight that our best control device matches the highest reported stabilized PCE for planar PSCs (~19%).<sup>[23,24]</sup> Therefore, with MAF we are improving the state-of-the-art, reaching a new record for planar PSC with 19.5% stabilized PCE.

In order to investigate the origin of the improved performances with the MAF, we performed intensity modulated photocurrent spectroscopy.<sup>[25]</sup> In Figure 5, we report the imaginary component frequency spectra of the current response to the light intensity modulated (10% of the stationary value) around 100 mW cm<sup>-2</sup> for devices with and without MAF. The spectra show three main features, which have been already reported by Baena *et al.* for similar planar PSCs.<sup>[26]</sup> The peak at low frequency (0.1 Hz - 100 Hz) has been correlated to the resonant frequencies of the ions and ion vacancies migration within the perovskite lattice. Here, we note that the peak of the MAF device is shifted towards higher frequency, indicating a faster ion migration. This is in line with the trend reported by Baena *et al.*, who demonstrated ions migrating faster in perovskite films composed of larger grains. Moving to higher frequency, there are two more peaks that have been assigned to the resonant frequencies of the charge dynamics within the perovskite and the other device components, such as the hole and the electron transporting layers. While the peak at highest frequency (fast charge dynamics) is rather similar with and without MAF, the peak at intermediated frequency (1 kHz - 100 KHz) is clearly visible only in the control and almost vanishes in the

MAF device. As we have previously shown, this peak provides information on the slow charge transport dynamics within the device.<sup>[27]</sup> The fact that its intensity is significantly lower suggests that the slow charge transport pathways are inhibited by the MAF. This behavior correlates with the crystal size distribution we presented in Figure 2b, where we showed that MAF reduces the formation of grains smaller than 150nm, which represent a great portion of the size distribution in the film without the MAF. The cross-sectional SEM images (see SI) of a perovskite film with MAF shows that larger grains can cross the whole thickness of the perovskite film, thus forming a sort of local single crystalline devices. The charge transport through a single crystal is significantly faster than through the grain boundaries of a polycrystalline film.<sup>[28,29]</sup> Therefore, inhibiting the formation of small crystals eliminates the slow charge transport pathways, which results in better device performances.

In conclusion, we reported planar perovskite solar cells with a record stabilized power conversion efficiency of 19.5%. We demonstrated that controlling the grain size distribution within the perovskite film is crucial to improve the state-of-the-art device. We made use of a specific ionic liquid, methylammonium formate, to retard the perovskite crystal growth in order to form a compact layer with larger grain sizes. XRD analysis showed that MAF induces a preferential growth of the perovskite crystals along the plane of the substrate. Planar perovskite solar cells prepared with MAF exhibited more effective charge transport, which results in higher power conversion efficiency compared to the state-of-the-art devices. Using ionic liquids to control the morphology of the perovskite film is a simple, general and effective method to enhance the efficiency of planar perovskite solar cells. Further advances are expected from using other ionic liquids that can selectively interact with the different elements composing the perovskite crystals.

**Experimental methods**

*Chemicals and Reagents.* All reagents except methylammonium formate and solvents were purchased from commercial sources and used without further purification unless otherwise noted.

*Chemical characterization.*  $^1\text{H}$  NMR spectra were obtained using a Bruker spectrometer (400 MHz) is reported in ppm using DMSO-d as an internal standard. X-ray powder (XRD) diagrams were recorded on an X'Pert MPD PRO (Panalytical) equipped with a ceramic tube (Cu anode,  $\lambda = 1.54060 \text{ \AA}$ ), a secondary graphite (002) monochromator and a RTMS X'Celerator (Panalytical). in an angle range of  $2\theta = 10^\circ$  to  $40^\circ$ .

*Methylammonium formate* (MAF) was synthesized using a previously reported procedure.<sup>[17]</sup>  $\text{CH}_3\text{NH}_3(\text{HCOO})$  was synthesized by dropping slowly 6 mL of formic acid (88wt% in water) in methanol to a solution of 20 mL methylamine (40wt% in water) in 10 mL absolute ethanol cooled at  $0^\circ\text{C}$ . After mixing reagent, the solution was further stirred for 1hr at  $0^\circ\text{C}$  under vacuum. Then the solution dried at room temperature under vacuum for 2 days.  $^1\text{H}$  NMR (400 MHz, DMSO-d): 2.30 (s, 3H), 8.40 (s, 1H) 8.64 (s, 3H).

*Solar cells fabrication.* Devices were fabricated on fluorine doped tin oxide (FTO) coated glass substrates. The substrates were cleaned sequentially with Hellmanex in ultrasonic bath for 30 min, then washed with acetone, isopropanol and finally cleaned with oxygen plasma for 5 min. Electron selective layer preparation F:SnO<sub>2</sub> substrates were cleaned first with acetone, then for 10 min in piranha solution ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  3: 1 v:v) and then for 10 min in a plasma cleaner prior to ALD deposition. SnO<sub>2</sub> was deposited at  $118^\circ\text{C}$  using tetrakis(dimethylamino)- tin(IV) (TDMASn, 99.99%-Sn, Strem Chemicals INC) and ozone at a constant growth rate of 0.065 nm per cycle measured by ellipsometry. TDMASn was held at  $65^\circ\text{C}$ . Ozone was produced using an ozone generator (AC-2025, IN USA Incorporated) fed

with oxygen gas (99.9995% pure, Carbagas) producing a concentration of 13% ozone in oxygen. Nitrogen was used as a carrier gas (99.9999% pure, Carbagas) with a flow rate of 10 sccm., before perovskite deposition, the pre-made ALD layers were treated with UV ozone for 10 min to remove by-products from the deposition process. The perovskite films were deposited from a precursor solution containing MAI(1.1M, Dyesol) and PbI<sub>2</sub>(1.1M, TCI Chemicals) in anhydrous DMSO (Acros) for MAPbI<sub>3</sub>, FAI (1.1 M, Dyesol), PbI<sub>2</sub> (1.2 M, TCI Chemicals), MABr (0.2 M, Dyesol) and PbBr<sub>2</sub> (0.2 M, TCI Chemicals) in anhydrous DMF:DMSO 4 : 1 (v/v, Acros) for mixed perovskite. Then home-made methylammonium formate (MAF) was added to perovskite solution as the amount, 5mole% of perovskite. The spin coating program includes two steps, first 1000 rpm for 10 s with a ramp of 200 rpm s<sup>-1</sup>, then 6000 rpm for 30 s with a ramp of 2000 rpm s<sup>-1</sup>. 15 s before the end of the spin-coating program, chlorobenzene was gently dropped on the spinning substrate. The substrate was then heated at 100°C for 1 hr on a hotplate in the nitrogen-filled glovebox. The HTM was subsequently deposited on the top of the perovskite layer by spin coating from solution at 4000 rpm for 20 s with a ramp of 2000 rpm s<sup>-1</sup>. The HTM solution was prepared by dissolving the compounds (spiro-OMeTAD) in chlorobenzene at concentration of 70 mM, with the addition of 50 mol% of bis(trifluoromethanesulfonyl)imide (Aldrich) from a stock solution of 1.8 M in acetonitrile, 330 mol% of tert-butylpyridine (Aldrich) and 3mol% of Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) Tris(bis(trifluoromethylsulfonyl)imide) (Dyesol) from a stock solution 0.25 M in acetonitrile. Finally, 80 nm gold layer was deposited by thermal evaporation under high vacuum, using a shadow masking to pattern the electrodes.

*Perovskite film characterization.* A ZEISS Merlin HR-SEM was used to characterize the morphology of the device top view and cross-section. X-ray powder (XRD) diagrams were recorded on an X'Pert MPD PRO (Panalytical) equipped with a ceramic tube (Cu anode,  $\lambda =$



1.54060 Å), a secondary graphite (002) monochromator and a RTMS X'Celerator (Panalytical). in an angle range of  $2\theta = 10^\circ$  to  $40^\circ$ . Absorption spectral measurements were recorded using Varian Cary5 UV–visible spectrophotometer. Photoluminescence spectra were obtained with Florolog 322 (Horiba Jobin Yvon Ltd) with the range of wavelength from 620 to 850nm by exciting at 460nm. The samples were mounted at  $60^\circ$  and the emission recorded at  $90^\circ$  from the incident beam path. For NMR analysis, the mixed perovskite films with/without MAF sintered at  $100^\circ\text{C}$  was rinsed with butanol for 1 minute in the gloves box after cooling down at  $25^\circ\text{C}$  to remove residual MAF and then dried on hotplate  $100^\circ\text{C}$  to evaporate solvent. Dried film was scratched to powder, which was dissolving in  $\text{D}_2\text{O}$ .

*Solar cell characterization.* Current-voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450 W xenon lamp (Oriel) equipped with a SchottK113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cut-off filter (KG-3, Schott). The scan rate was  $10\text{ mV s}^{-1}$ . Maximum power point tracking was performed with Keithley model 2400 driven by a homemade algorithm developed in Igorpro software. The cell was initially biased at 1 V. The bias voltage was decreased of 5mV each 500 ms towards the maximum power point. For each voltage step the algorithm evaluates if the derivative of the power over the time is positive or negative. If the derivative is positive the scan direction remains the same. On the contrary the algorithm changes direction if the derivative is negative. When the bias voltage reaches the maximum power point the applied bias oscillates within 10-15 mV perturbing and observing continuously the solar cell under illumination. IPCE spectra were recorded as functions of wavelength under a constant white light bias of approximately  $10\text{ mW cm}^{-2}$  supplied by an

array of white light emitting diodes. The excitation beam coming from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at approximately 2 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems). All measurements were conducted using a non-reflective metal aperture of 0.16 cm<sup>2</sup> to define the active area of the device and avoid light scattering through the sides. Intensity modulated photocurrent spectroscopy was performed using Autolab PGSTAT302N according to procedures previously reported.<sup>[25]</sup>

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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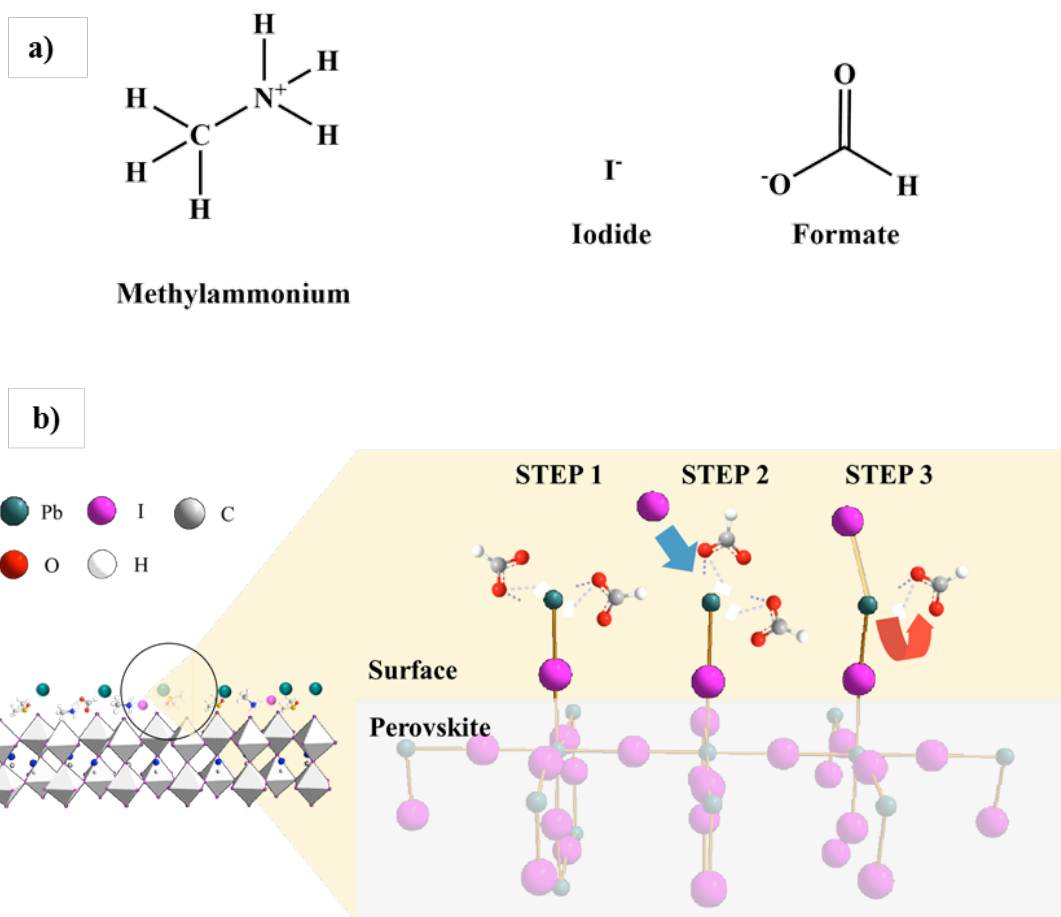
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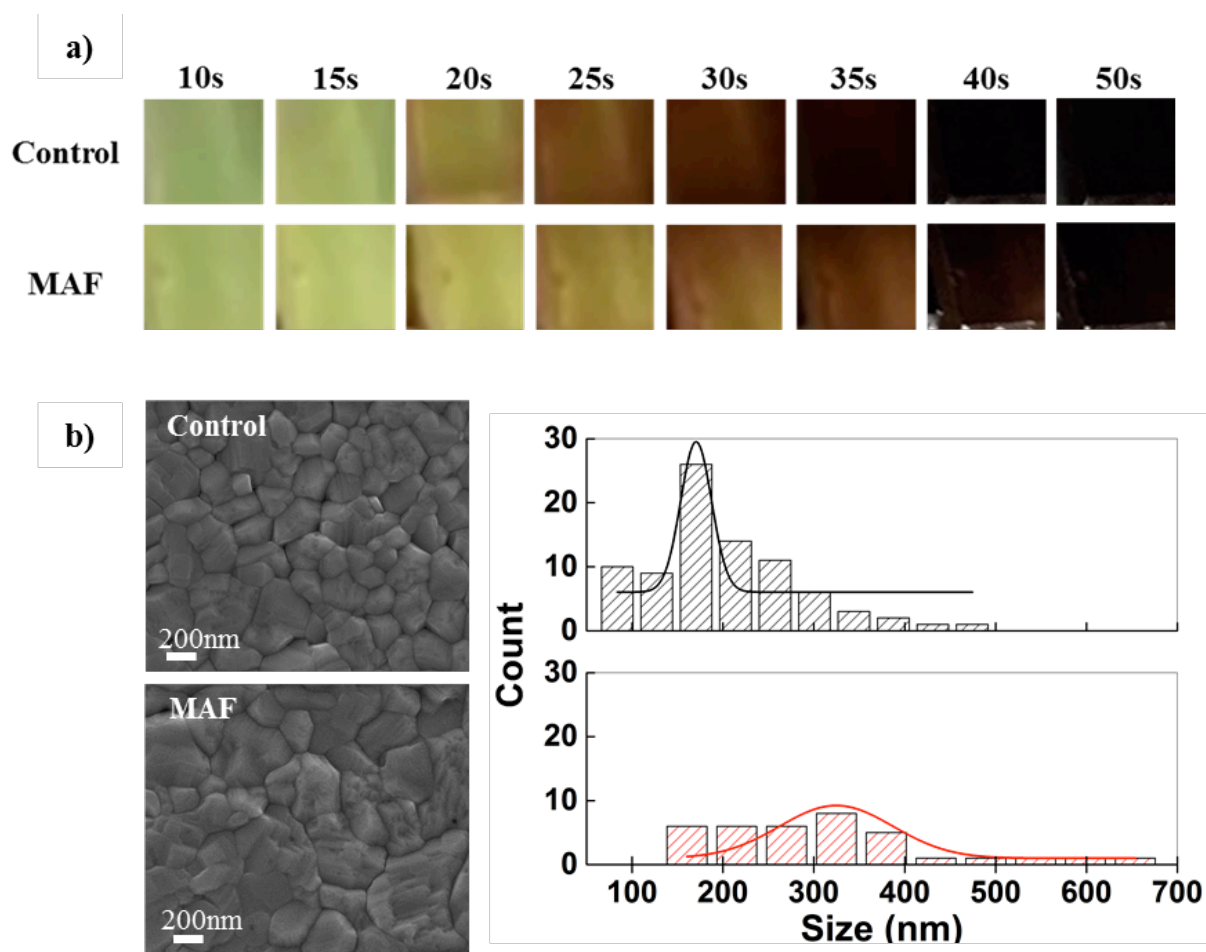
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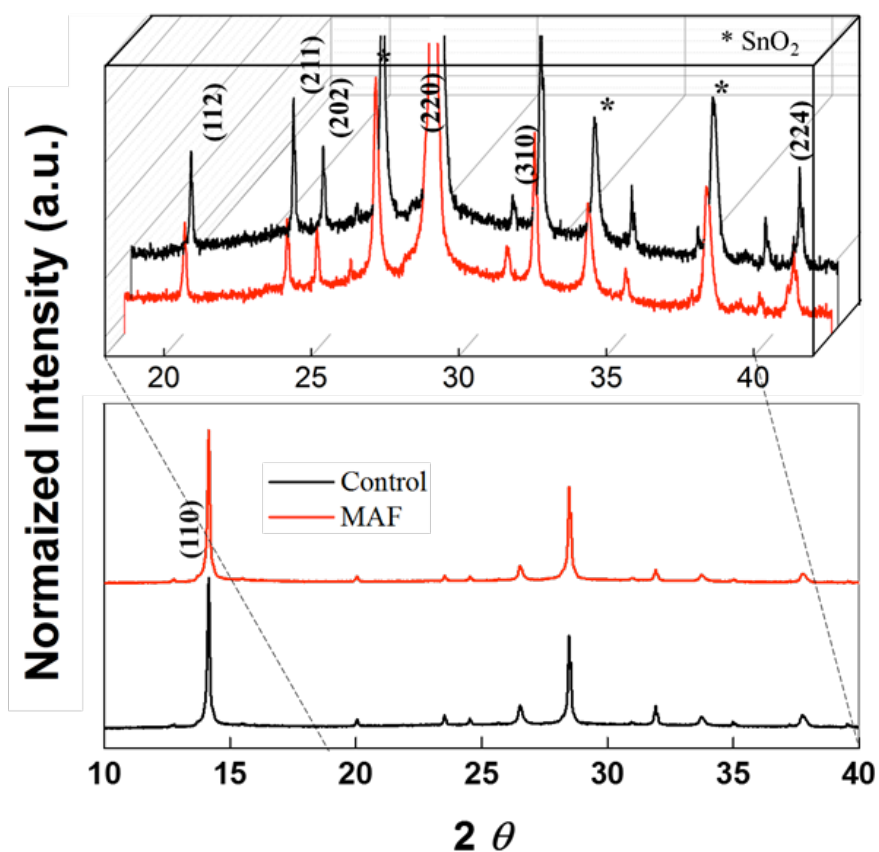
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**Figure 1.** a) Molecular structure of the organic precursors methylammonium iodide and formate. b) Schematic of the proposed perovskite crystal growth mechanism as controlled by the formate anions.

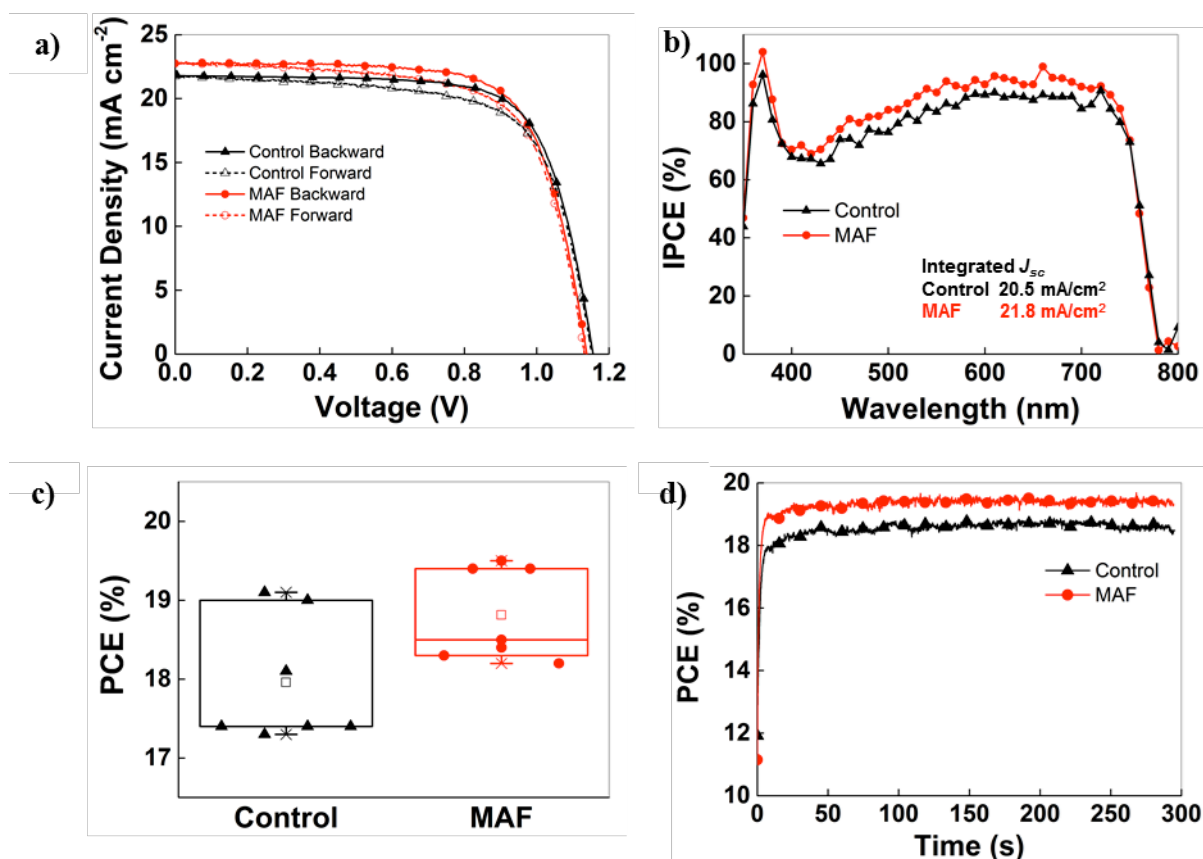


**Figure 2.** Morphological analysis of the perovskite films with and without MAF. a) Pictures of perovskite films collected at subsequent delay times after posing the substrates on a hotplate at 100°C. b) (left) Top-view SEM images of perovskite films after 1hr annealing at 100°C. (right) Grain sizes distribution as estimated from the SEM images using Nano measurer 1.2 software.

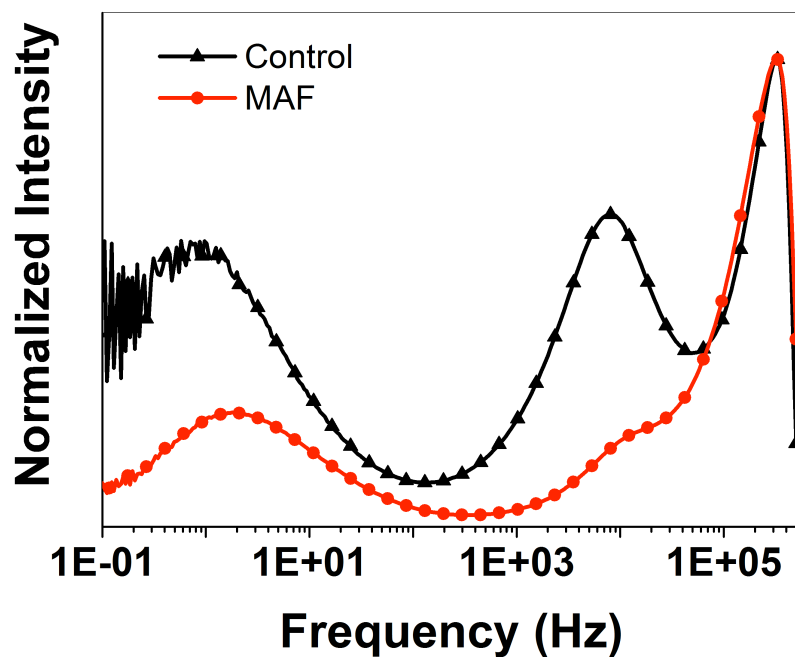


**Figure 3.** X-ray diffraction diagram of perovskite films deposited on  $\text{SnO}_2$  substrates with and without MAF, the intensity is normalized to the peak at  $14^\circ$  (110). Inset: enlarged spectra displaying the relative intensities of the peaks between  $18^\circ$  and  $42^\circ$ .





**Figure 4.** Photovoltaic metrics of perovskite solar cells prepared with and without MAF. a)  $J-V$  curves were measured from forward bias to short circuit condition and vice versa at the scan rate of  $10 \text{ mV/s}$  under AM1.5 simulated solar light ( $94.8 \text{ mW/cm}^2$ ). The device active area was defined using a black metal shadow mask with an aperture of  $0.16 \text{ cm}^2$ . b) Incident photon-to-current efficiency (IPCE) curve (solid line) and the integrated photocurrent (dashed line) for the MAF device. c) Box plot of the PCE collected from 7 devices. d) Maximum power conversion efficiency as function of time was extracted from the maximum power point tracking under AM1.5 simulated solar light.



**Figure 5.** Imaginary component frequency spectra of the current response to the light intensity modulated around  $100 \text{ mW cm}^{-2}$  for devices with and without MAF. The intensities are normalized to the maximum value.

**Table 1.** Photovoltaic parameters of best devices with and without MAF: open-circuit voltage ( $V_{oc}$ ), short circuit current ( $J_{sc}$ ), fill factor (FF), power conversion efficiency as extracted from the J-V curves (PCE, backward and forward scan) and from the stabilized maximum power point (Stab. PCE) in Figure 5.

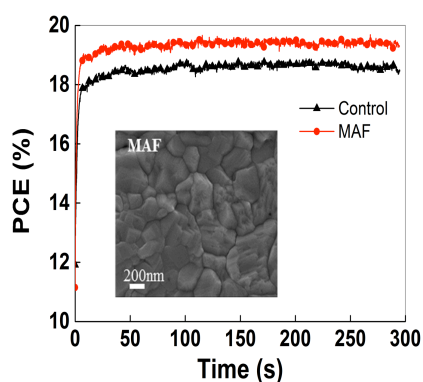
	Scan Direction	$J_{sc}$ mA cm <sup>-2</sup>	$V_{oc}$ V	FF	PCE %	Stab. PCE % after 60s
<b>Control</b>	Backward	21.7	1.16	0.72	19.1	<b>18.9</b>
	Forward	21.7	1.15	0.69	18.1	
<b>MAF</b>	Backward	22.7	1.14	0.71	19.5	<b>19.5</b>
	Forward	22.7	1.13	0.69	18.6	

**Ionic liquids to retard the perovskite crystal growth, aiming for a compact perovskite layer with larger grains.** We present an ionic liquid driven mechanism of crystal growth and we demonstrate that the larger perovskite grains enable more effective charge collection and thus better solar cell performances with a record stabilized PCE of 19.5

**ionic liquids; morphology control; planar perovskite solar cell; hysteresis; mixed halide perovskite; photovoltaics.**

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**Ionic liquid control crystal growth to enhance planar perovskite solar cells efficiency**



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